

SM
5/23/97
Title: 3-(Het)arylcarboxylic Acid Derivatives

62 Rec'd PCT/PTO

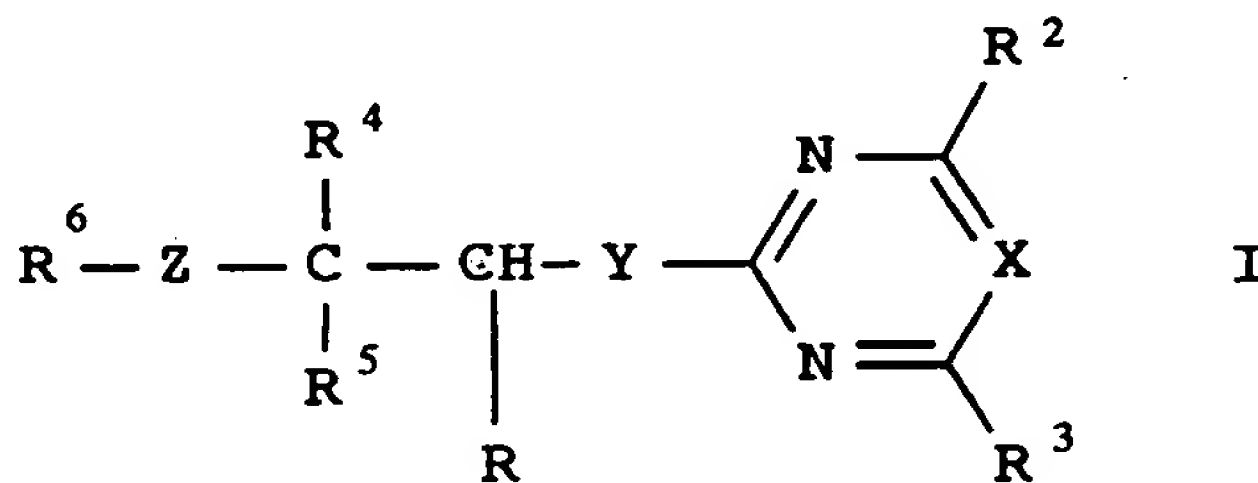
19 OCT 1995

This application has been filed under 35 USC 371 as a national stage application of PCT/EP94/01141, filed April 13, 1994.

~~3-(Het)arylcarboxylic acid derivatives, their preparation and intermediates for their preparation.~~

Background of the Invention

5 3-(het)arylcarboxylic acid derivatives of the general formula I



15 where R is formyl, CO₂H or a radical hydrolyzable to COOH, and the other substituents have the following meanings:

R² is halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio;

20

X is nitrogen or CR¹⁴, where R¹⁴ is hydrogen or, together with R³, forms a 3-membered or 4-membered alkylene or alkenylene chain, in each of which a methylene group is replaced by oxygen;

25

R³ is halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio or R³ is linked to R¹⁴ as stated above to form a 5-membered or 6-membered ring;

30

R⁴ is phenyl or naphthyl which may be substituted by one or more, in particular one to three of the following radicals: halogen, nitro, cyano, hydroxyl, mercapto, amino, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylamino, di-C₁-C₄-alkylamino, C₁-C₄-alkyl-carbonyl or C₁-C₄-alkoxycarbonyl;

35

a five-membered or six-membered heteroaromatic structure which contains one to three nitrogen atoms and/or one sulfur or oxygen atom and may carry one or more of the following radicals: halogen, nitro, cyano, hydroxyl, mercapto, amino, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylamino, C₁-C₄-dialkylamino, C₁-C₄-alkylcarbonyl, C₁-C₄-alkoxycarbonyl or phenyl;

40

45

2

- R⁵ is hydrogen, C₁-C₄-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl, C₃-C₈-cycloalkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxyalkyl, C₁-C₄-alkylthioalkyl or phenyl;
- 5 R⁶ is C₁-C₈-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl or C₃-C₈-cycloalkyl, it being possible for these radicals to be mono- or polysubstituted in each case by: halogen, nitro, cyano, C₁-C₄-alkoxy, C₃-C₆-alkenyloxy, C₃-C₆-alkynyloxy, C₁-C₄-alkylthio, C₁-C₄-haloalkoxy, C₁-C₄-alkylcarbonyl, C₁-C₄-alkoxy-
- 10 carbonyl, C₁-C₄-alkylamino, di-C₁-C₄-alkylamino, phenyl or phenyl or phenoxy which is mono- or polysubstituted; for example mono- to trisubstituted, by halogen, nitro, cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio;
- 15 Y is sulfur or oxygen or a single bond; and
- Z is sulfur or oxygen;
- 20 with the proviso that R⁶ is not unsubstituted C₁-C₄-alkyl when R⁴ is unsubstituted phenyl, Z is oxygen and simultaneously R⁵ is methyl or hydrogen.

The prior art, eg. EP-A 347 811, EP-A 400 741, EP-A 409 368, EP-A 481 512, EP-A 517 215, Chemical Abstracts, 119, No. 139 254e (1993), and the prior German application P 41 42 570 (EP-A-548 710), describes similar carboxylic acid derivatives, including 3-alkoxy derivatives but not those which carry a het(aryl) radical in the 3 position.

B 30 *SUMMARY OF THE INVENTION*
Since the herbicidal and/or bioregulatory action and selectivity of the known compounds is not always satisfactory, it is an object of the present invention to provide compounds having better selectivity and/or better biological activity.

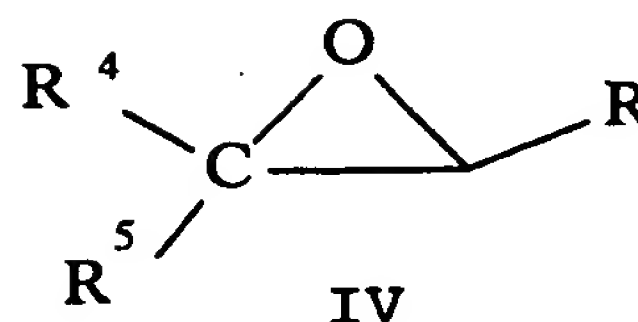
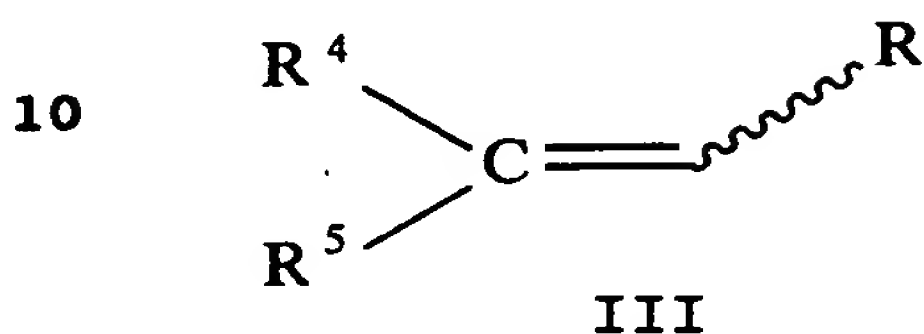
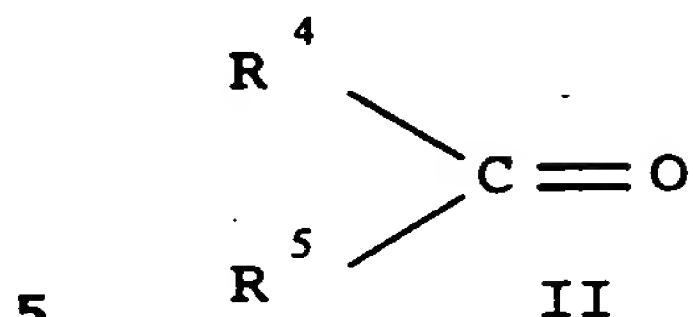
35 We have found that this object is achieved and that the 3-(het)arylcarboxylic acid derivatives defined at the outset have excellent herbicidal and plant growth-regulating properties. Furthermore, the compounds I have good pharmacological efficacy,

40 particularly in the cardiovascular sector.

The preparation of the novel compounds starts from the epoxides IV, which are obtained in a generally known manner, as described, for example, in J. March, Advanced Organic Chemistry, 2nd ed.,

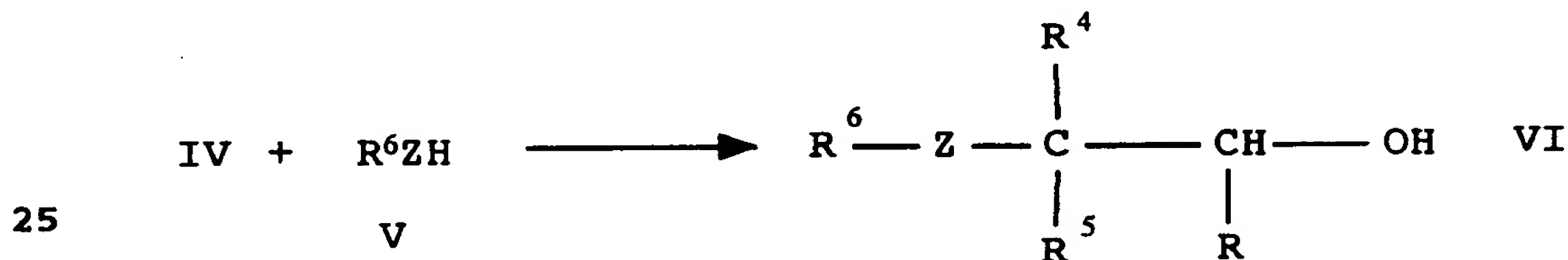
45 1983, page 862 and page 750, from the aldehydes or ketones II or the olefins III:

3



15 3-(Het)arylcarmxylic acid derivatives of the general formula VI can be prepared by reacting the epoxide of the general formula IV (for example, with $R = ROOR^{10}$) with alcohols or thiols of the general formula V, where R^6 and Z have the meanings stated in claim 1.

20



30 For this purpose, compounds of the general formula IV are heated with an excess of the compounds of the formula V, for example with 1.2-7, preferably 2-5, mole equivalents, to 50 - 200°C, preferably 80 - 150°C.

35 The reaction can also be carried out in the presence of a diluent. All solvents which are inert to the reagents used may be employed for this purpose.

40 Examples of such solvents or diluents are water, aliphatic, alicyclic and aromatic hydrocarbons, each of which may be chlorinated, for example hexane, cyclohexane, petroleum ether, naphtha, benzene, toluene, xylene, methylene chloride, chloroform, carbon tetrachloride, ethylene chloride and trichloroethylene, ethers, such as diisopropyl ether, dibutyl ether, propylene oxide, dioxane and tetrahydrofuran, ketones, for example acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone, 45 nitriles, such as acetonitrile and propionitrile, alcohols, such as methanol, ethanol, isopropanol, butanol and ethylene glycol, esters, for example ethyl acetate and amyl acetate, amides, such

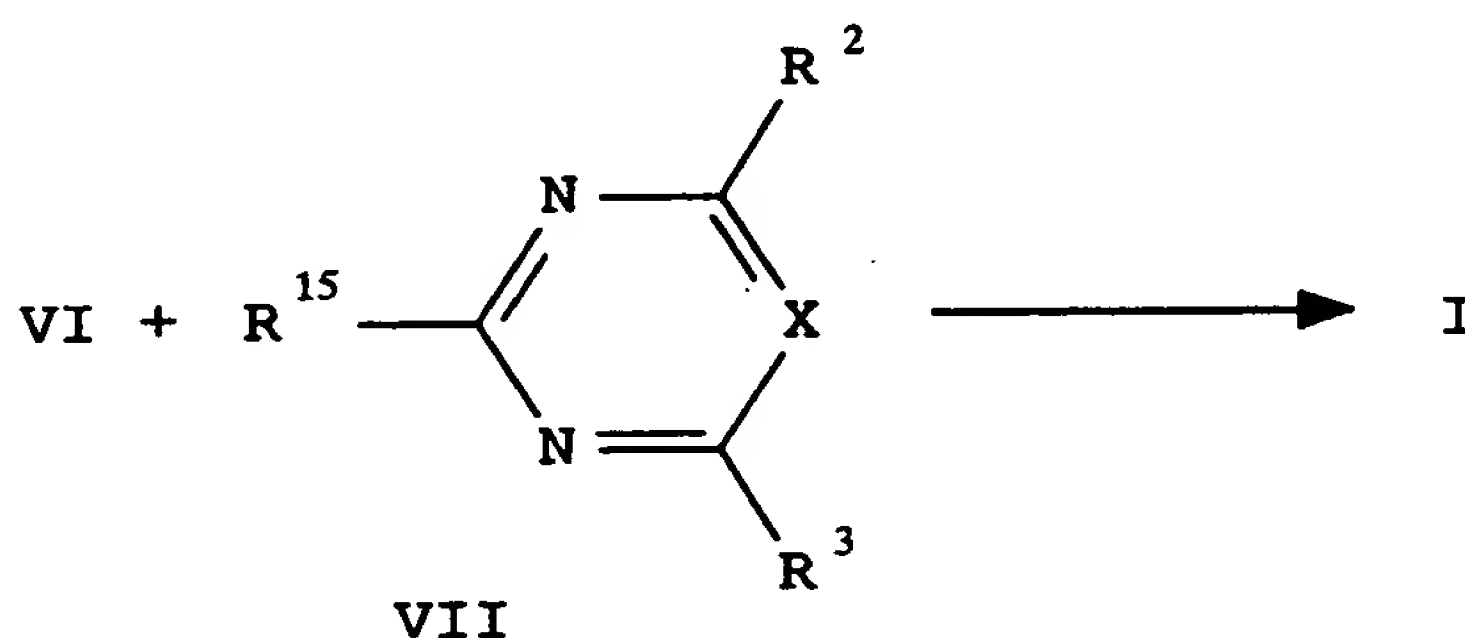
as dimethylformamide and dimethylacetamide, sulfoxides and sulfones, for example dimethyl sulfoxide and sulfolane, and bases, such as pyridine.

- 5 The reaction is preferably carried out at from 0°C to the boiling point of the solvent or solvent mixture.

The presence of a catalyst for the reaction may be advantageous. Suitable catalysts are strong organic and inorganic acids and
10 Lewis acids. Examples of these include sulfuric acid, hydrochloric acid, trifluoroacetic acid, boron trichloride etherate and titanium(IV) alcoholates.

The novel compounds in which Y is oxygen and the remaining substituents have the meanings stated under the general formula I
15 can be prepared, for example, by reacting the 3-(het)aryl-carboxylic acid derivatives of the general formula VI in which the substituents have the stated meanings with compounds of the general formula VII

20



30

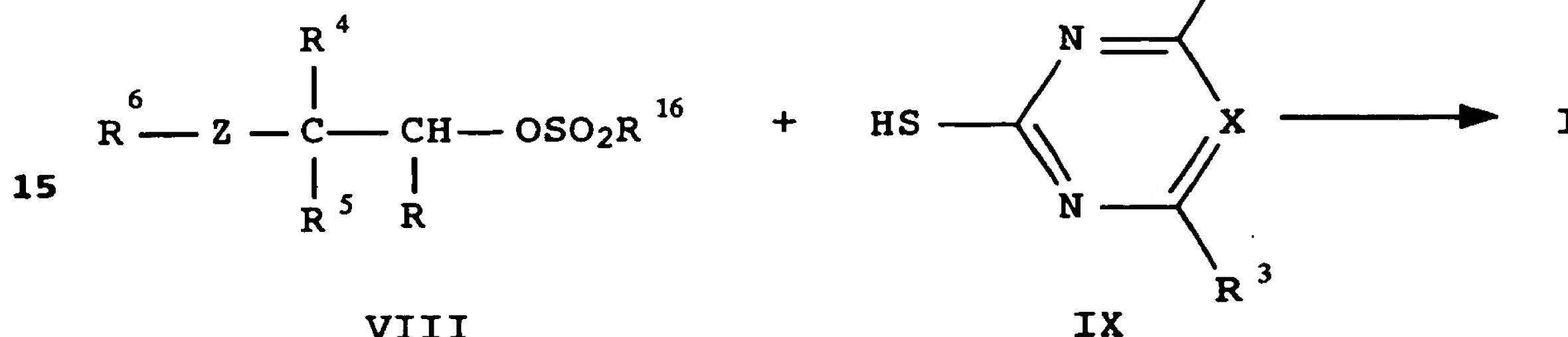
where R¹⁵ is halogen or R¹⁶-SO₂- and R¹⁶ may be C₁-C₄-alkyl, C₁-C₄-haloalkyl or phenyl. The reaction is preferably carried out in one of the abovementioned inert diluents with the addition of a suitable base, ie. a base which effects deprotonation of the
35 intermediate VI, at from room temperature to the boiling point of the solvent.

The bases may be an alkali metal or alkaline earth metal hydride, such as sodium hydride, potassium hydride or calcium hydride, a
40 carbonate, such as an alkali metal carbonate, for example, sodium carbonate or potassium carbonate, an alkali metal or alkaline earth metal hydroxide, such as sodium hydroxide or potassium hydroxide, an organometallic compound, such as butyllithium, or an alkali metal amide, such as lithium diisopropylamide.

45

The novel compounds in which Y is sulfur and the remaining substituents have the meanings stated under the general formula I can be prepared, for example, by reacting 3-(het)arylcarboxylic acid derivatives of the general formula VIII, which are obtain-
 5 able in a known manner from compounds of the general formula VI and in which the substituents have the abovementioned meanings, with compounds of the general formula IX where R², R³ and X have the meanings stated under the general formula I.

10



20 The reaction is preferably carried out in one of the above-mentioned inert diluents with the addition of a suitable base, ie. a base which effects deprotonation of the intermediate IX, at from room temperature to the boiling point of the solvent.

25 The bases used may be organic bases, such as tertiary amines, for example triethylamine, pyridine, imidazole or diazabicyclo-undecene, in addition to the abovementioned bases.

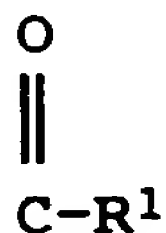
Compounds of the formula I can also be prepared by starting from
 30 the corresponding carboxylic acids, ie. compounds of the formula I in which R¹ is hydroxyl, and first converting these in a conventional manner into an activated form, such as a halide, an anhydride or an imidazolid, and then reacting this with a corresponding hydroxyl compound HOR¹⁰. This reaction can be
 35 carried out in the conventional solvents and often requires the addition of a base, the abovementioned bases being suitable. These two steps can also be simplified, for example, by allowing the carboxylic acid to act on the hydroxy compound in the presence of a water-eliminating agent, such as a carbodiimide.

40

In addition, compounds of the formula I can also be prepared by starting from the salts of the corresponding carboxylic acids, ie. from compounds of the formula I in which R is COR¹ and R¹ is OM, where M may be an alkali metal cation or one equivalent of an
 45 alkaline earth metal cation. These salts can be reacted with many compounds of the formula R¹-A, where A is a conventional nucleofugic leaving group, for example halogen, such as chlorine,

bromine or iodine, or aryl- or alkylsulfonyl which is unsubstituted or substituted by halogen, alkyl or haloalkyl, eg. toluenesulfonyl and methylsulfonyl, or another equivalent leaving group. Compounds of the formula R^1-A having a reactive substituent A are known or can be readily obtained on the basis of general technical knowledge. The reaction can be carried out in the conventional solvents and is effected advantageously with the addition of a base, the abovementioned bases being suitable.

R in the formula I can be widely varied. For example, R is a group



where R^1 has the following meanings:

- a) hydrogen,
- b) a succinylimidoxy group;
- c) a 5-membered heteroaromatic structure which is bonded via a nitrogen atom, such as pyrrolyl, pyrazolyl, imidazolyl or triazolyl, and which may carry one or two halogen atoms, in particular fluorine or chlorine and/or one or two of the following radicals:
- C_1-C_4 -alkyl, such as methyl, ethyl, 1-propyl, 2-propyl, 2-methyl-2-propyl, 2-methyl-1-propyl, 1-butyl or 2-butyl;
- C_1-C_4 -haloalkyl, in particular C_1 - or C_2 -haloalkyl, for example fluoromethyl, difluoromethyl, trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trichloromethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trifluoroethyl or pentafluoroethyl;
- C_1-C_4 -haloalkoxy, in particular C_1 - or C_2 -haloalkoxy, such as difluoromethoxy, trifluoromethoxy, chlorodifluoromethoxy, 1-fluoroethoxy, 2-fluoroethoxy, 2,2-difluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-1,1,2-trifluoroethoxy or pentafluoroethoxy, in particular trifluoromethoxy;

C₁-C₄-alkoxy, such as methoxy, ethoxy, propoxy, 1-methylethoxy, butoxy, 1-methylpropoxy, 2-methylpropoxy or 1,1-dimethylethoxy, in particular methoxy, ethoxy or 1-methylethoxy;

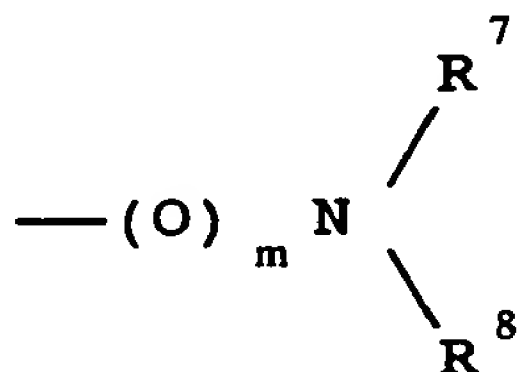
5

C₁-C₄-alkylthio, such as methylthio, ethylthio, propylthio, 1-methylethylthio, butylthio, 1-methylpropylthio, 2-methylpropylthio or 1,1-dimethylethylthio, in particular methylthio or ethylthio;

10

d) R¹ is furthermore a radical

15



20

where m is 0 or 1 and R⁷ and R⁸ may be identical or different and have the following meanings:

hydrogen;

25

C₁-C₈-alkyl, in particular C₁-C₄-alkyl as tested above;

30

C₃-C₆-alkenyl, such as 2-propenyl, 2-butenyl, 3-butenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-2-butenyl, 2-methyl-3-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-2-propenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl,

35

3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl,

40

1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-tri-

45

methyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl or

1-ethyl-2-methyl-2-propenyl, in particular 2-propenyl, 2-butenyl, 3-methyl-2-butenyl or 3-methyl-2-pentenyl;

5 C₃-C₆-alkynyl such as 2-propynyl, 2-butyne, 3-butyne, 1-methyl-2-propynyl, 2-pentyne, 3-pentyne, 4-pentyne, 1-methyl-3-butyne, 2-methyl-3-butyne, 1-methyl-2-butyne, 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-pentyne, 1-methyl-2-pentyne, 1-methyl-3-pentyne, 10 1-methyl-4-pentyne, 2-methyl-3-pentyne, 2-methyl-4-pentyne, 3-methyl-4-pentyne, 4-methyl-2-pentyne, 1,1-dimethyl-2-butyne, 1,1-dimethyl-3-butyne, 1,2-dimethyl-3-butyne, 2,2-dimethyl-3-butyne, 1-ethyl-2-butyne, 1-ethyl-3-butyne, 15 2-ethyl-3-butyne or 1-ethyl-1-methyl-2-propynyl, preferably 2-propynyl, 2-butyne, 1-methyl-2-propynyl or 1-methyl-2-butyne, in particular 2-propynyl;

20 C₃-C₈-cycloalkyl, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or cycloheptyl, cyclooctyl, where these alkyl, cycloalkyl, alkenyl and alkynyl groups may each carry one to five halogen atoms, in particular fluorine or chlorine, and/or one or two of the following groups:

25 C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-alkylthio, C₁-C₄-haloalkoxy as stated above, C₃-C₆-alkenyloxy, C₃-C₆-alkenylthio, C₃-C₆-alkynyloxy, or C₃-C₆-alkynylthio, where the alkenyl and alkynyl moieties present in these radicals preferably have the abovementioned meanings;

30 C₁-C₄-alkylcarbonyl, in particular methylcarbonyl, ethylcarbonyl, propylcarbonyl, 1-methylethylcarbonyl, butylcarbonyl, 1-methylpropylcarbonyl, 2-methylpropylcarbonyl, 1,1-dimethylethylcarbonyl;

35 C₁-C₄-alkoxycarbonyl, such as methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, 1-methylethoxycarbonyl, butoxycarbonyl, 1-methylpropoxycarbonyl, 2-methylpropoxycarbonyl, 1,1-dimethylethoxycarbonyl;

40 C₃-C₆-alkenylcarbonyl, C₃-C₆-alkynylcarbonyl, C₃-C₆-alkenyloxy-carbonyl or C₃-C₆-alkynyloxy-carbonyl, where the alkenyl and alkynyl radicals are preferably defined as stated individually above;

45

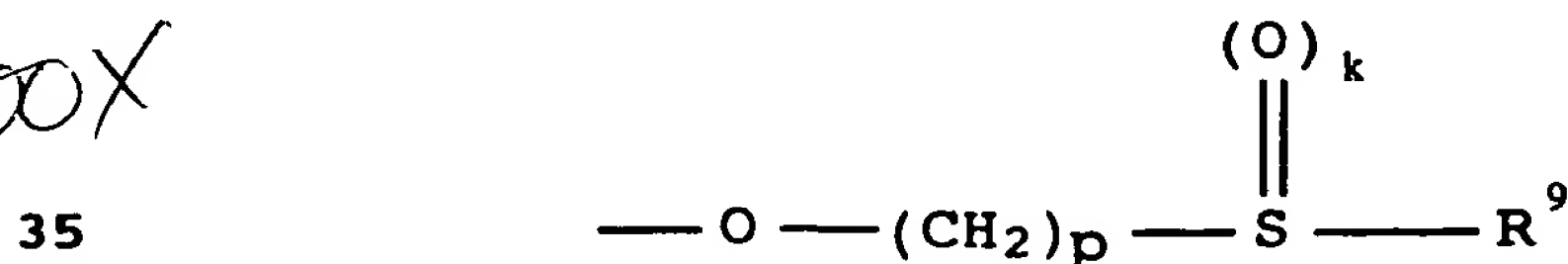
phenyl, unsubstituted or monosubstituted or polysubstituted, for example monosubstituted to trisubstituted, by halogen, nitro, cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio, for example 2-fluorophenyl, 3-chlorophenyl, 4-bromophenyl, 2-methylphenyl, 3-nitrophenyl, 4-cyanophenyl, 2-trifluoromethylphenyl, 3-methoxyphenyl, 4-trifluoroethoxyphenyl, 2-methylthiophenyl, 2,4-dichlorophenyl, 2-methoxy-3-methylphenyl, 2,4-dimethoxyphenyl, 2-nitro-5-cyanophenyl or 2,6-difluorophenyl;

di-C₁-C₄-alkylamino, in particular dimethylamino, dipropylamino, N-propyl-N-methylamino, N-propyl-N-ethylamino, diisopropylamino, N-isopropyl-N-methylamino, N-isopropyl-N-ethylamino or N-isopropyl-N-propylamino;

R⁷ and R⁸ are each furthermore phenyl, which may be substituted by one or more, for example one to three, of the following radicals: halogen, nitro, cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio, as stated in particular above;

or R⁷ and R⁸ together form a cyclic, optionally substituted, for example C₁-C₄-alkyl-substituted, C₄-C₇-alkylene chain which may contain a heteroatom selected from the group consisting of oxygen, sulfur and nitrogen, such as -(CH₂)₄-, -(CH₂)₅-, -(CH₂)₆-, -(CH₂)₇-, -(CH₂)₂-O-(CH₂)₂-, -CH₂-S-(CH₂)₃-, -(CH₂)₂-O-(CH₂)₃-, -NH-(CH₂)₃-, -CH₂-NH-(CH₂)₂-, -CH₂-CH=CH-CH₂- or -CH=CH-(CH₂)₃-;

30 e) R¹ is furthermore a group



where k is 0, 1 or 2, p is 1, 2, 3 or 4 and R⁹ is

C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl or unsubstituted or substituted phenyl, as stated in particular above.

f) R¹ is furthermore a radical OR¹⁰, where R¹⁰ is:

hydrogen, the cation of an alkali metal, such as lithium, sodium or potassium, or the cation of an alkaline earth metal, such as calcium, magnesium or barium, or an

environmentally compatible organic ammonium ion, such as tertiary C₁-C₄-alkylammonium or the ammonium ion;

5 C₃-C₈-cycloalkyl as stated above, which may carry one to three C₁-C₄-alkyl groups;

10 C₁-C₈-alkyl, in particular methyl, ethyl, propyl, 1-methyl-ethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethyl-ethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,1,2-trimethylpropyl, 15 1,2,2-trimethylpropyl, 1-ethylbutyl, 2-ethylbutyl, 1-ethyl-2-methylpropyl, which may carry one to five halogen atoms, in particular fluorine or chlorine, and/or one of the following radicals:

20 C₁-C₄-alkoxy, C₁-C₄-alkylthio, cyano, C₁-C₄-alkylcarbonyl, C₃-C₈-cycloalkyl [sic], C₁-C₄-alkoxycarbonyl, phenyl, phenoxy or phenylcarbonyl, where the aromatic radicals in turn may each carry one to five halogen atoms and/or one to three of the following radicals: nitro, cyano, C₁-C₄-alkyl, C₁-C₄-halo- 25 alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy and/or C₁-C₄-alkylthio, as stated in particular above;

30 C₁-C₈-alkyl as stated above, which may carry one to five halogen atoms, in particular fluorine and/or chlorine, and carries one of the following radicals: a 5-membered hetero-aromatic structure which contains one to three nitrogen atoms, or a 5-membered heteroaromatic structure which contains one nitrogen atom and one oxygen or sulfur atom and which may carry one to four halogen atoms and/or one or two 35 of the following radicals:

40 nitro, cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, phenyl, C₁-C₄-haloalkoxy and/or C₁-C₄-alkylthio. Particular examples are: 1-pyrazolyl, 3-methyl-1-pyrazolyl, 4-methyl-1-pyrazolyl, 3,5-dimethyl-1-pyrazolyl, 3-phenyl-1-pyrazolyl, 4-phenyl-1-pyrazolyl, 4-chloro-1-pyrazolyl, 4-bromo-1-pyrazolyl, 1-imidazolyl, 1-benzimidazolyl, 1,2,4-triazol-1-yl, 3-methyl-1,2,4-triazol-1-yl, 5-methyl-1,2,4-triazol-1-yl, 1-benzotriazolyl, 3-isopropylisoxazol-5-yl, 3-methyl- 45 isoxazol-5-yl, oxazol-2-yl, thiazol-2-yl, imidazol-2-yl,

11

3-ethylisoxazol-5-yl, 3-phenylisoxazol-5-yl, 3-tert-butylisoxazol-5-yl;

5 C₂-C₆-alkyl which carries one of the following radicals in the 2 position: C₁-C₄-alkoxyimino, C₃-C₆-alkynyloxyimino, C₃-C₆-haloalkenyloxyimino or benzyloxyimino;

C₃-C₆-alkenyl or C₃-C₆-alkynyl, where these groups in turn may carry one to five halogen atoms;

10

R¹⁰ is furthermore phenyl which may carry one to five halogen atoms and/or one to three of the following radicals: nitro, cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy and/or C₁-C₄-alkylthio, as stated in particular above;

15

a 5-membered heteroaromatic structure which is bonded via a nitrogen atom, contains one to three nitrogen atoms and may carry one or two hydrogen atoms and/or one or two of the following radicals: C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy,

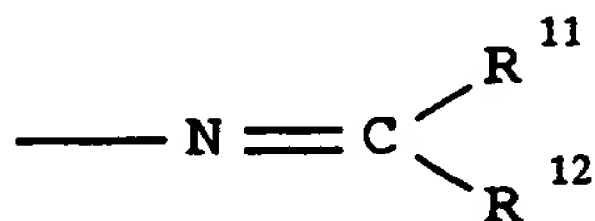
20

phenyl, C₁-C₄-haloalkoxy and/or C₁-C₄-alkylthio. Particular examples are 1-pyrazolyl, 3-methyl-1-pyrazolyl, 4-methyl-1-pyrazolyl, 3,5-dimethyl-1-pyrazolyl, 3-phenyl-1-pyrazolyl, 4-phenyl-1-pyrazolyl, 4-chloro-1-pyrazolyl, 4-bromo-1-pyrazolyl, 1-imidazolyl, 1-benzimidazolyl, 1,2,4-triazol-1-yl, 3-methyl-1,2,4-triazol-1-yl, 5-methyl-1,2,4-triazol-1-yl, 1-benzotriazolyl and 3,4-dichloroimidazol-1-yl;

25

R¹⁰ is furthermore a group

30



where R¹¹ and R¹² may be identical or different and are each:

35

C₁-C₈-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl or C₃-C₈-cycloalkyl, where these radicals may carry C₁-C₄-alkoxy, C₁-C₄-alkylthio and/or unsubstituted or substituted phenyl, as stated in particular above;

40

phenyl, which may be substituted by one or more, for example one to three, of the following radicals: halogen, nitro, cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio, where these radicals correspond in particular to the abovementioned ones;

45

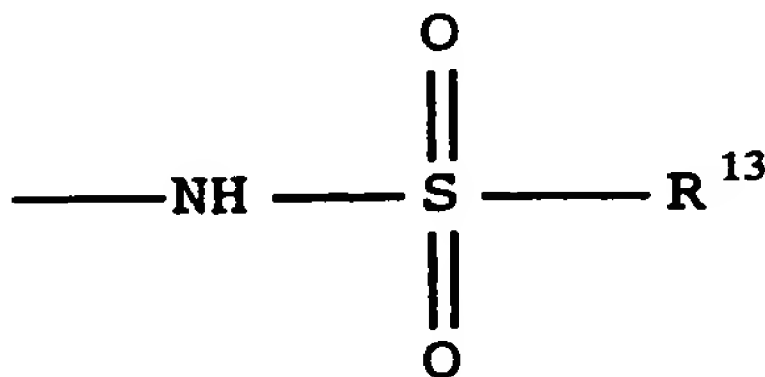
or R¹¹ and R¹² together form a C₃-C₁₂-alkylene chain which may carry one to three C₁-C₄-alkyl groups and may contain a heteroatom selected from the group consisting of oxygen, sulfur and nitrogen, as stated in particular for R⁷ and R⁸.

5

g) R¹ is furthermore a radical

10

T130X



where R¹³ is:

15

C₁-C₄-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl, C₃-C₈-cycloalkyl as stated in particular above, where these radicals may carry C₁-C₄-alkoxy, C₁-C₄-alkylthio and/or phenyl as stated above;

20

phenyl, unsubstituted or substituted, in particular as stated above.

With regard to the biological activity, preferred 3-(het)aryl-oxy(thio)carboxylic acid derivatives are those of the general
25 formula I in which the substituents have the following meanings:

R² is one of the C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio groups stated individually in the case of R¹ or is halogen, in particular chlorine,
30 methyl, methoxy, ethoxy, difluoromethoxy, trifluoromethoxy or particularly preferably methoxy;

X is nitrogen or CR¹⁴, where

35 R¹⁴ is hydrogen or, together with R³, forms a 4-membered or 5-membered alkylene or alkenylene chain, in each of which a methylene group is replaced by oxygen, such as -CH₂-CH₂-O-, -CH=CH-O-, -CH₂-CH₂-CH₂-O- or -CH=CH-CH₂O- [sic], in particular hydrogen or -CH₂-CH₂-O-;

40

R³ is one of the C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio groups stated in the case of R¹ or is halogen, in particular chlorine, methyl, methoxy, ethoxy, difluoromethoxy, trifluoromethoxy or is bonded to R¹⁴
45 as stated above to form a 5-membered or 6-membered ring, R³ is particularly preferably methoxy;

R⁴ is 5-membered or 6-membered heteroaryl, such as furyl, thienyl, pyrrolyl, pyrazolyl, imidazolyl, triazolyl, isoxazolyl, oxazolyl, isothiazolyl, thiazolyl, thiadiazolyl, pyridyl, pyrimidinyl, pyrazinyl, pyridazinyl, triazinyl, for example 2-furanyl, 3-furanyl, 2-thienyl, 3-thienyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 5-imidazolyl, 2-pyrrolyl, 3-pyrrolyl, 3-pyrrolyl, [sic] 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, oxa-2,4-diazolyl, oxa-3,4-diazoylyl [sic], thia-2,4-diazolyl, thia-3,4-diazolyl or triazolyl, where the heteroaromatic structures may carry one to five halogen atoms as stated above, in particular fluorine or chlorine and/or one to three of the following radicals:

C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-alkylthio, cyano, nitro, C₁-C₈-alkylcarbonyl, C₁-C₈-alkoxycarbonyl, phenyl, phenoxy or phenylcarbonyl as stated in general and in particular above;

R⁴ is furthermore phenyl or naphthyl, each of which may be substituted by one or more, eg. one to three, of the following radicals: halogen, nitro, cyano, hydroxyl, mercapto, amino, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylamino or di-C₁-C₄-alkylamino, C₁-C₄-alkylcarbonyl, C₁-C₄-alkoxycarbonyl, in particular as stated in the case of R⁷ and R⁸ or for example 3-hydroxyphenyl, 4-dimethylaminophenyl, 2-mercapto-phenyl, 3-methoxycarbonylphenyl, 4-acetylphenyl, 1-naphthyl, 2-naphthyl, 3-bromo-2-naphthyl, 4-methyl-1-naphthyl, 5-methoxy-1-naphthyl, 6-trifluoromethyl-1-naphthyl [sic], 7-chloro-1-naphthyl or 8-hydroxy-1-naphthyl;

R⁵ is hydrogen, C₁-C₄-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl, C₃-C₇-cycloalkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxyalkyl, C₁-C₄-alkylthioalkyl or phenyl as stated above in particular for R⁴;

R⁶ is C₁-C₈-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl or C₃-C₈-cycloalkyl as stated in particular above, each of which may be mono- to polysubstituted by the following radicals: halogen, nitro, cyano, C₁-C₄-alkoxy, C₃-C₆-alkenyloxy, C₃-C₆-alkynyl-oxy, C₁-C₄-alkylthio, C₁-C₄-haloalkoxy, C₁-C₄-alkylcarbonyl, C₁-C₄-alkoxycarbonyl, C₁-C₄-alkylamino or di-C₁-C₄-alkylamino or unsubstituted or substituted phenyl or phenoxy, as stated in particular above;

14

14

Y is sulfur, oxygen or a single bond and

Z is sulfur or oxygen,

5 with the proviso that R^6 is not unsubstituted C_1-C_4 -alkyl when R^4 is unsubstituted phenyl, Z is oxygen and simultaneously R^5 is methyl or hydrogen.

10 Compounds of the formula I where R^2 and R^3 are each methoxy and X is CH are particularly preferred. Examples of preferred compounds are listed in the following table. The definitions given for R^4 there and in Tables 1 and 2 are likewise to be regarded as preferred, irrespective of the definitions of radicals in combination with R^4 .

15

20

25

30

35

40

45

16

T/60X

Table

R ¹	R ⁴	R ⁵	R ⁶	R ²	R ³	X	Y	Z
OH	Phenyl	Methyl	Methyl	OCH ₃	OCH ₃	CH	S	S
OH	Phenyl	Methyl	Methyl	OCH ₃	OCH ₃	CH	O	S
OCH ₃	Phenyl	Methyl	Methyl	OCH ₃	OCH ₃	CH	S	S
OH	Phenyl	i-Propyl	Methyl	OCH ₃	OCH ₃	CH	O	O
OCH ₃	2-Fluorophenyl	Ethyl	Methyl	OCH ₃	OCH ₃	CH	O	O
OC ₂ H ₅	3-Chlorophenyl	Propyl	Methyl	OCH ₃	OCH ₃	N	O	O
ON(CH ₃) ₂	4-Bromophenyl	i-Propyl	Methyl	CF ₃	CF ₃	CH	S	O
ON=C(CH ₃) ₂	2-Thienyl	Methyl	Methyl	OCF ₃	OCF ₃	CH	O	S
HNSO ₂ C ₆ H ₅	3-Thienyl	Methyl	Methyl	CH ₃	CH ₃	CH	O	O
NHPhenyl	2-Furyl	Methyl	Methyl	Cl	Cl	CH	O	O
ONa	3-Furyl	Methyl	Methyl	OCH ₃	-OCH ₂ -CH ₂ -		S	O
O-CH ₂ -C≡CH	Phenyl	Ethyl	Ethyl	OCH ₃	CF ₃	CH	O	O
OH	Phenyl	Propyl	Propyl	OCH ₃	OCF ₃	CH	O	S
OCH ₃	Phenyl	i-Propyl	i-Propyl	OCH ₃	CH ₃	CH	O	O
OC ₂ H ₅	Phenyl	Methyl	s-Butyl	OCH ₃	Cl	CH	S	O
ON(CH ₃) ₂	2-Methylphenyl	Methyl	Methyl	OCH ₃	OCH ₃	CH	O	O
ON(CH ₃) ₂	3-Methoxyphenyl	Methyl	Methyl	OCH ₃	OCH ₃	CH	O	O
ON=C(CH ₃) ₂	4-Nitrophenyl	Methyl	Methyl	OCH ₃	OCH ₃	CH	O	O
NHPhenyl	2-Oxazolyl	Methyl	Methyl	CF ₃	CF ₃	N	S	O
ONa	4-Oxazolyl	Methyl	Propen-3-yl	OCF ₃	OCF ₃	N	O	S

R ¹	R ⁴	R ⁵	R ⁶	R ²	R ³	X	Y	Z
O-CH ₂ -C≡CH	5-Oxazolyl	Methyl	Propyn-3-yl	CH ₃	CH ₃	N	O	O
OH	3-Isoxazolyl	Methyl	Cyclopentyl	Cl	Cl	N	O	O
OCH ₃	4-Isoxazolyl	Methyl	Cyclohexyl	OCH ₃	-O-CH ₂ -CH ₂ -		O	O
OC ₂ H ₅	5-Isoxazolyl	Methyl	Cyclopropylmethyl	OCH ₃	CF ₃	N	S	O
ON(CH ₃) ₂	Phenyl	Methyl	1-Phenylpropyl-3-yl	OCH ₃	OCF ₃	N	O	S
ON=C(CH ₃) ₂	2-Hydroxyphenyl	Methyl	Methyl	OCH ₃	CH ₃	N	O	O
ONSO ₂ C ₆ H ₅	3-Trifluoromethyl-phenyl	Methyl	Methyl	OCH ₃	Cl	N	O	O
NHPhenyl	4-Dimethylamino-phenyl	Methyl	Methyl	OCH ₃	OCH ₃	CH	S	O
ONa	2-Imidazolyl	Ethyl	Methyl	OCH ₃	OCH ₃	CH	S	S
O-CH ₂ -C≡CH	4-Imidazolyl	Propyl	Methyl	OCH ₃	OCH ₃	N	S	S
OH	3-Pyrazolyl	i-Propyl	Methyl	CF ₃	CF ₃	CH	O	S
OCH ₃	4-Pyrazolyl	Methyl	Methyl	OCF ₃	OCF ₃	CH	O	O
OC ₂ H ₅	Phenyl	Methyl	Trifluoroethyl	CH ₃	CH ₃	CH	O	O
ON(CH ₃) ₂	Phenyl	Methyl	Benzyl	Cl	Cl	CH	O	O
ON(CH ₃) ₂	Phenyl	Methyl	2-Methoxyethyl	OCH ₃	-O-CH ₂ -CH ₂ -		S	O
ON=C(CH ₃) ₂	Phenyl	Methyl	3-Methoxycarbonyl-propyl	OCH ₃	CF ₃	N	S	S
NH-Phenyl	2-Pyridyl	Methyl	2-Chloroethyl	OCH ₃	OCF ₃	N	S	S
ONa	3-Pyridyl	Methyl	Methyl	OCH ₃	CH ₃	N	O	O
O-CH ₂ -C≡CH	4-Pyridyl	Methyl	Methyl	OCH ₃	Cl	N	O	O

The compounds I and the herbicides containing them and their environmentally compatible salts of alkali metals and alkaline earth metals ensure very good control of weeds and grass weeds in crops such as wheat, rice and corn, soybean and cotton, without damaging the crops, an effect which occurs in particular at low application rates.

They may be applied, for example, in the form of directly spray-
10 able solutions, powders, suspensions, including concentrated aqueous, oily or other suspensions or dispersions, emulsions, oil dispersions, pastes, dusting agents, broadcasting agents or granules, by spraying, nebulizing, dusting, broadcasting or pouring. The application forms depend on the intended uses; they
15 should in any case ensure a very fine distribution of the novel active ingredients.

The compounds I are suitable in general for the preparation of directly sprayable solutions, emulsions, pastes or oil disper-
20 sions. Suitable inert additives include mineral oil fractions having a medium to high boiling point, such as kerosine or diesel oil, and coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, eg. toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or
25 derivatives thereof, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, chlorobenzene, isophorone or strongly polar solvents, such as N,N-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone or water.

30 Aqueous application forms can be prepared from emulsion concentrates, dispersions, pastes, wettable powders or water-dispersible granules by adding water. For the preparation of emulsions, pastes or oil dispersions, the substrates [sic] as such are dissolved in an oil or solvent, can be homogenized in
35 water by means of wetting agents, adherents, dispersants or emulsifiers. However, it is also possible to prepare concentrates which consist of active ingredient, wetting agents, adherents, dispersants or emulsifiers and possibly solvents or oil and which are suitable for dilution with water.

40

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of aromatic sulfonic acids, for example lignin-sulfonic, phenolsulfonic, naphthalenesulfonic and dibutyl-naphthalenesulfonic acid, and of fatty acids, alkanesulfonates,
45 alkylarylsulfonates, alkylsulfates, lauryl ether sulfates and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols and of fatty alcohol glycol ethers, condensates of

sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of naphthalene sulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctyl-, octyl- or nonylphenyl, alkylphenyl poly-
5 glycol ether, tributylphenyl polyglycol ether, alkylaryl poly-
ether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide
condensates, ethoxylated castor oil, polyoxyethylene alkyl ether
or polyoxypropylene [lacuna], lauryl alcohol polyglycol ether
acetate, sorbitol esters, lignin sulfite waste liquors or methyl
10 cellulose.

Powders, broadcasting agents and dusting agents can be prepared by mixing or milling the active ingredients together with a solid carrier.

15

Granules, for example coated, impregnated and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Solid carriers are mineral earths such as silicas, silica gels, silicates, talc, kaolin, limestone, lime,
20 chalk, bole, loess, clay, dolomite, kieselguhr, calcium sulfate,
magnesium sulfate, magnesium oxide, milled plastics, fertilizers, such as ammonium sulfate, ammonium phosphate, ammonium nitrate and ureas, and vegetable products, such as grain flour, bark meal, wood meal and nutshell meal, cellulosic powders and other
25 solid carriers.

The formulations contain in general from 0.01 to 95, preferably from 0.5 to 90, % by weight of active ingredient. The active ingredients are used in the purity of from 90 to 100 %, prefer-
30 ably from 95 to 100 % (according to the NMR spectrum).

Examples of formulations are:

I. 20 parts by weight of compound No. 2.1 are dissolved in a
35 mixture which consists of 80 parts by weight of alkylated
benzene, 10 parts by weight of the adduct of from 8 to
10 mol of ethylene oxide with 1 mol of N-monoethanol-
oleamide, 5 parts by weight of the calcium salt of
dodecylbenzenesulfonic acid and 5 parts by weight of the
40 adduct of 40 mol of ethylene oxide with 1 mol of castor
oil. By pouring the solution into 100,000 parts by weight
of water and finely distributing it therein, an aqueous
dispersion which contains 0.02 % by weight of the active
ingredient is obtained.

45

- II. 20 parts by weight of compound No. 2.1 are dissolved in a mixture which consists of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 mol of ethylene oxide with 1 mol of isooctylphenol and 10 parts by weight of the adduct of 40 mol of ethylene oxide with 1 mol of castor oil. By pouring the solution into 100,000 parts by weight of water and finely distributing it therein, an aqueous dispersion which contains 0.02 % by weight of the active ingredient is obtained.
- III. 20 parts by weight of active ingredient No. 2.1 are dissolved in a mixture which consists of 25 parts by weight of cyclohexanone, 65 parts by weight of a mineral oil fraction boiling within the range from 210 to 280°C and 10 parts by weight of the adduct of 40 mol of ethylene oxide with 1 mol of castor oil. By pouring the solution into 100,000 parts by weight of water and finely distributing it therein, an aqueous dispersion which contains 0.02 % by weight of the active ingredient is obtained.
- IV. 20 parts by weight of active ingredient No. 2.1 are thoroughly mixed with 3 parts by weight of the sodium salt of diisobutyl-naphthalene- α -sulfonic acid, 17 parts by weight of the sodium salt of a ligninsulfonic acid obtained from a sulfite waste liquor and 60 parts by weight of silica gel powder, and the mixture is milled in a hammer mill. By finely distributing the mixture into 20,000 parts by weight of water, a spray liquor which contains 0.1 % by weight of the active ingredient is obtained.
- V. 3 parts by weight of active ingredient No. 2.1 are mixed with 97 parts by weight of finely divided kaolin. A dusting agent which contains 3 % by weight of the active ingredient is obtained in this manner.
- VI. 20 parts by weight of active ingredient No. 2.1 are thoroughly mixed with 2 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, 8 parts by weight of a fatty alcohol polyglycol ether, 2 parts by weight of the sodium salt of a phenol/urea/formaldehyde condensate and 68 parts by weight of a paraffinic mineral oil. A stable oily dispersion is obtained.

Application can be carried out by the preemergence or post-emergence method. If the active ingredients are less well tolerated by certain crops, it is possible to use application methods in which the herbicides are sprayed with the aid of the
5 sprayers so that the leaves of the sensitive crops are as far as possible not affected while the active ingredients reach the leaves of undesirable plants growing underneath or the uncovered soil surface (post-directed, lay-by).

10 The application rates of active ingredient are from 0.001 to 5, preferably from 0.01 to 2, kg/ha of active ingredient (a.i.), depending on the aim of control, the season, the target plants and the stage of growth.

15 In view of the versatility of the application methods, the novel compounds or the agents containing them can be used in a further number of crops for eliminating undesirable plants. Examples of suitable crops are the following:

20 *Allium cepa*, *Ananas comosus*, *Arachis hypogaea*, *Asparagus officinalis*, *Beta vulgaris* spp. *altissima*, *Beta vulgaris* spp. *rapa*, *Brassica napus* var. *napus*, *Brassica napus* var. *napobrassica*, *Brassica rapa* var. *silvestris*, *Camellia sinensis*, *Carthamus tinctorius*, *Carya illinoensis*, *Citrus limon*, *Citrus*
25 *sinensis*, *Coffea arabica* (*Coffea canephora*, *Coffea liberica*), *Cucumis sativus*, *Cynodon dactylon*, *Daucus carota*, *Elaeis guineensis*, *Fragaria vesca*, *Glycine max*, *Gossypium hirsutum* (*Gossypium arboreum*, *Gossypium herbaceum*, *Gossypium vitifolium*), *Gossypium hirsutum* (*Gossypium arboreum*, *Gossypium*, [sic]
30 *herbaceum*, *Gossypium vitifolium*), *Helianthus annuus*, *Hevea brasiliensis*, *Hordeum vulgare*, *Humulus lupulus*, *Ipomoea batatas*, *Juglans regia*, *Lens culinaris*, *Linum usitatissimum*, *Lycopersicon lycopersicum*, *Malus* spp., *Manihot esculenta*, *Medicago sativa*, *Musa* spp., *Nicotiana tabacum* (*N. rustica*), *Olea europaea*, *Oryza*
35 *sativa*, *Phaseolus lunatus*, *Phaseolus vulgaris*, *Picea abies*, *Pinus* spp., *P. isum* [sic] *sativum*, *Prunus avium*, *Prunus persica*, *Pyrus communis*, *Ribes sylvestre*, *Ricinus communis*, *Saccharum officinarum*, *Secale cereale*, *Solanum tuberosum*, *Sorghum bicolor* (*S. vulgare*), *Theobroma cacao*, *Trifolium pratense*, *Triticum aestivum*,
40 *Triticum durum*, *Vicia faba*, *Vitis vinifera*, *Zea mays*.

The compounds of the formula I can influence virtually all development stages of a plant in different ways and are therefore used as growth regulators. The diversity of action of the plant
45 growth regulators depends in particular

a) on the plant species and variety,

21

- b) on the time of application, based on the state of development of the plants and on the season
- c) on the place of application and application method (for example seed dressing, soil treatment, foliar application or trunk injection in the case of trees),
- d) on climatic factors, for example temperature and amount of precipitation, as well as length of day and light intensity,
- e) on the soil characteristics (including fertilizer application),
- 10 f) on the formulation or application form of the active ingredient and finally
- g) on the concentration of active ingredient used.

From the many different potential applications of the plant growth regulators of the formula I in plant cultivation, in agriculture and in horticulture, some are mentioned below.

- A. With the compounds which can be used according to the invention, it is possible greatly to inhibit the vegetative growth of the plants, which is evident in particular from a reduction in the growth in length.

Accordingly, the treated plants exhibit stunted growth; moreover, a darker leaf coloration is observed.

- A reduced intensity of the growth of grasses and crops susceptible to lodging, such as cereals, corn, sunflowers and soybean, proves advantageous in practice. Shortening and strengthening of the stems reduce or eliminate the danger of lodging of plants under unfavorable weather conditions prior to harvesting.

- The use of growth regulators for inhibiting the growth in length and for changing the time of ripening in the case of cotton is also important. This permits completely mechanized harvesting of this important crop.

- In the case of fruit trees and other trees, pruning costs can be saved by means of the growth regulators. Moreover, the alternation of fruit trees can be broken by means of growth regulators.

- By using growth regulators, it is also possible to increase or inhibit the lateral branching of the plants. This is of interest when, for example in the case of tobacco plants, the

formation of side shoots is to be inhibited in favor of foliar growth.

5 Growth regulators can also be used for considerably
increasing the resistance to frost, for example in the case
of winter rape. On the one hand, the growth in length and the
development of foliage and plant mass which is too luxurious
(and therefore particularly susceptible to frost) are
10 inhibited. On the other hand, after sowing and prior to the
onset of the winter frost, the young rape plants are held
back in the vegetative stage of development in spite of
favorable growth conditions. This also eliminates the danger
of frost for plants which tend to exhibit premature cessation
15 of inhibition of blooming and to grow over into the genera-
tive phase. In other crops too, for example winter cereals,
it is advantageous if, through treatment with the novel
compounds in the fall, the stocks are well tillered but do
not start the winter with too luxurious a growth. A greater
20 sensitivity to frost and - owing to the relatively small
foliage or plant mass - attack by various diseases (for
example fungal disease) can thus be prevented.

B. The growth regulators can be used to achieve high yields of
both plant parts and plant ingredients. For example, it is
25 possible to induce the growth of larger amounts of buds,
flowers, leaves, fruits, seed kernels, roots and tubers, to
increase the content of sugar in sugarbeets, sugar cane and
citrus fruits, to increase the protein content of cereals or
soybean or to stimulate rubber trees to produce greater latex
30 flow.

The compounds of the formula I can result in higher yields by
intervening in the plant metabolism or by promoting or
inhibiting vegetative and/or generative growth.

35 C. Finally, plant growth regulators can be used both for
shortening and lengthening the stages of development and for
accelerating or slowing down the ripening of the harvested
plant parts before or after harvesting.

40 For example, facilitating harvesting, which is made possible
by concentrated dropping or a reduction in the adhesion to a
tree in the case of citrus fruits, olives or other species
and varieties of pomes, drupes and indehiscent fruit, is of
45 commercial interest. The same mechanism, ie. promotion of the
formation of abscission tissue between fruit or leaf and stem

part of the plant is also essential for readily controllable defoliation of crops such as cotton.

- D. The growth regulators can furthermore reduce the water consumption of plants. By using the novel substances, it is possible to reduce the intensity of irrigation and hence to carry out more economical farming because, inter alia,
- the extent of opening of the stomata is reduced,
 - a thicker epidermis and cuticle are formed,
 - the root penetration of the soil is improved and
 - the microclimate in the plant stock is favorably influenced by more compact growth.
- Compounds I are particularly suitable for shortening the stems of crops such as barley, rape and wheat.

The active ingredients of the formula I which are to be used according to the invention can be fed to the crops both via the seed (as seed dressing) and via the soil, ie. through the roots and - particularly preferably - via the foliage by spraying.

The application rate of active ingredient is not critical, owing to the high tolerance by plants. The optimum application rate varies depending on the aim of control, the season, the target plants and the stages of growth.

In the case of seed treatment, in general from 0.001 to 50, preferably from 0.01 to 10, g of active ingredient per kilogram of seed are required.

For foliage and soil treatment, in general doses of from 0.001 to 10, preferably from 0.01 to 3, in particular from 0.01 to 0.5, kg/ha are to be considered sufficient.

In order to broaden the action spectrum and to achieve synergistic effects, the compounds of the formula I may be mixed with many members of other groups of herbicidal or growth-regulating active ingredients and applied together with them. Suitable components of the mixture are, for example, diazines, 4H-3,1-benzoxazine derivatives, benzothiadiazinones, 2,6-dinitroanilines, N-phenylcarbamates, thiocarbamates, halocarboxylic acids, triazines, amides, ureas, diphenyl ethers, triazinones, uracils, benzofuran derivatives, cyclohexane-1,3-dione derivatives which carry, for example, a carboxyl or carbimino group in the 2 position, quinoline carboxylic acid derivatives, imidazolinones,

24

sulfonamides, sulfonylureas, aryloxy- and heteroaryloxyphenoxy-propionic acids and their salts, esters and amides and others.

It may also be useful to apply the compounds of the formula I,
5 alone or in combination with other herbicides, also as a mixture with further crop protection agents, for example with pesticides or agents for controlling phytopathogenic fungi or bacteria. The miscibility with mineral salt solutions which are used for eliminating nutrient and trace element deficiencies is also of
10 interest. Nonphytotoxic oils and oil concentrates may also be added.

B *DESCRIPTION OF THE Preferred Embodiments*
Synthesis examples

15 Synthesis of compounds of the general formula VI

Example 1

Methyl 3-methoxy-3-(3-methoxyphenyl)-2-hydroxybutyrate

20 19.5 g (88 mmol) of methyl 3-(3-methoxyphenyl)-2,3-epoxybutyrate are dissolved in 200 ml of absolute methanol, and 0.1 ml of boron trifluoride etherate is added. Stirring is carried out for 12 hours at room temperature and the solvent is distilled off. The residue is taken up in ethyl acetate and the solution is
25 washed with sodium bicarbonate solution and water and dried over sodium sulfate. After the solvent has been distilled off, 21.1 g of a slightly yellow oil remain.

Yield: 94 % (diastereomer mixture 1:1)

30

Example 2

Methyl 3-benzyloxy-3-phenyl-2-hydroxybutyrate

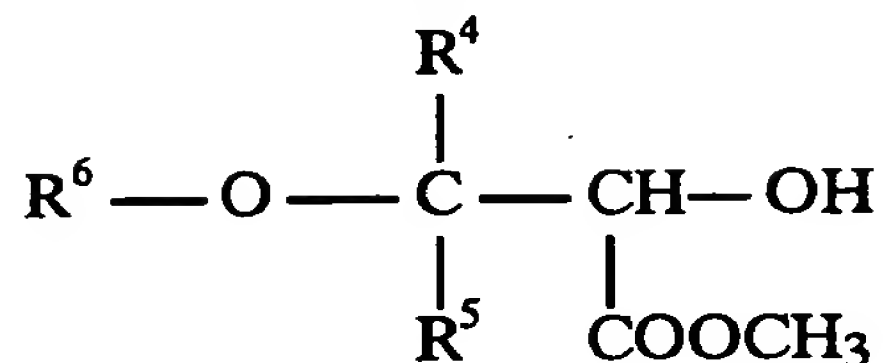
9.6 g (50 mmol) of methyl 3-phenyl-2,3-epoxybutyrate are dis-
35 solved in 150 ml of benzyl alcohol, and 0.5 ml of concentrated sulfuric acid is added. Stirring is carried for 6 hours at 50°C and the mixture is allowed to cool to room temperature. After neutralization with sodium bicarbonate solution, the excess benzyl alcohol is distilled off under greatly reduced pressure
40 and the residue is purified by flash chromatography over silica gel using 9:1 n-hexane/ethyl acetate. After the solvent has been distilled off, 6.5 g of a colorless oil remain.

Yield: 43 % (diastereomer mixture 3:2)

45

All the compounds stated in Table 1 are prepared similarly:

Table 1:

Intermediates of the formula VI where R¹ is CH₃

7260X 5

10	No.	R ⁶	R ⁴	R ⁵	DR*	Mp. [°C]
	1.1	Methyl	3-Methoxyphenyl	Methyl	1:1	oil
	1.2	Benzyl	Phenyl	Methyl	3:2	oil
	1.3	Methyl	2-Fluorophenyl	Methyl	1:1	oil
15	1.4	Methyl	4-i-Propylphenyl	Methyl		
	1.5	Methyl	2-Methylphenyl	Methyl	2:1	oil
	1.6	Methyl	3-Methylphenyl	Methyl		
	1.7	Methyl	4-Methylphenyl	Methyl	3:2	oil
	1.8	Methyl	3-Nitrophenyl	Methyl		
20	1.9	Methyl	4-Bromophenyl	Methyl	3:1	oil
	1.10	Methyl	2-Furyl	Methyl		
	1.11	Methyl	3-Furyl	Methyl		
	1.12	Methyl	2-Thienyl	Methyl		
	1.13	Methyl	3-Thienyl	Methyl		
25	1.14	Methyl	2-Pyridyl	Methyl		
	1.15	Methyl	3-Pyridyl	Methyl		
	1.16	Methyl	4-Pyridyl	Methyl		
	1.17	Methyl	2-Thiazolyl	Methyl		
	1.18	Methyl	3-Isoxazolyl	Methyl		
30	1.19	Methyl	4-Imidazolyl	Methyl		
	1.20	Methyl	2-Pyrazolyl	Methyl		
	1.21	Methyl	4-Chlorophenyl	Methyl	2:1	oil
	1.22	Benzyl	3-Methylphenyl	Methyl	1:1	oil
	1.23	Methyl	4-Fluorophenyl	Methyl	1:1	oil
35	1.24	Benzyl	4-Bromophenyl	Methyl	1:1	oil
	1.25	Benzyl	4-Chlorophenyl	Methyl	3:2	oil
	1.26	Benzyl	4-Fluorophenyl	Methyl	1:1	oil
	1.27	Methyl	Phenyl	Ethyl	1:1	oil
	1.28	Methyl	3-Nitrophenyl	Methyl	2:1	oil
40	1.29	Ethyl	4-Methylphenyl	Methyl	1:1	oil
	1.30	Benzyl	4-Methylphenyl	Methyl	1:1	oil
	1.31	Benzyl	Phenyl	Ethyl	1:0	oil
	1.32	4-Fluorobenzyl	Phenyl	Methyl	1:1	oil

45

* Diastereomer Ratio

26

Synthesis of compounds of the general formula I:

Example 3:

Methyl 3-benzyloxy-3-phenyl-2-(4,6-dimethoxypyrimidin-2-yloxy)-
5 butyrate

3 g (10 mmol) of methyl 3-benzyloxy-3-phenyl-2-hydroxybutyrate
(compound 1.1) are dissolved in 40 ml of dimethylformamide, and
0.3 g (12 mmol) of sodium hydride are added. Stirring is carried
10 out for 1 hour, after which 2.2 g (10 mmol) of 4,6-dimethoxy-
2-methylsulfonylpyrimidine are added. After stirring has been
carried out for 24 hours at room temperature, hydrolysis is ef-
fected carefully with 10 ml of water, the pH is brought to 5 with
acetic acid and the solvent is distilled off under greatly
15 reduced pressure. The residue is taken up in 100 ml of ethyl
acetate, washed with water and dried over sodium sulfate and the
solvent is distilled off. 10 ml of methyl tert-butyl ether are
added to the residue and the precipitate formed is filtered off
with suction. After drying, 2.4 g of a white powder remain.

20

Yield: 55 % (diastereomer mixture 1:1)

Mp.: 115 - 117°C

Example 4

25 3-Benzyloxy-3-phenyl-2-(4,6-dimethoxypyrimidin-2-yloxy)butyric
acid

1.4 g (3 mmol) of methyl 3-benzyloxy-3-phenyl-2-(4,6-dimethoxy-
pyrimidin-2-yloxy)butyrate (Example 3) are dissolved in 20 ml of
30 methanol and 20 ml of tetrahydrofuran, and 3.7 g of 10 % strength
NaOH solution are added. Stirring is carried out for 6 hours at
60°C and for 12 hours at room temperature, the solvent is
distilled off under reduced pressure and the residue is taken up
in 100 ml of water. Extraction is now carried out with ethyl
35 acetate to remove unconverted ester. The aqueous phase is then
brought to pH 1 - 2 with dilute hydrochloric acid and is
extracted with ethyl acetate. After drying has been carried out
over magnesium sulfate and the solvent has been distilled off, a
little acetone is added to the residue and the precipitate formed
40 is filtered off with suction. After drying, 1.2 g of a white
powder remain.

Yield: 88 %

Mp.: 165°C (decomposition, diastereomer mixture 3:2)

45

Example 5

Methyl 3-benzyloxy-3-phenyl-2-(4,6-dimethoxypyrimidin-2-ylthio)-butyrate

5

11 g (25 mmol) of methyl 3-benzyloxy-3-phenyl-2-hydroxybutyrate (compound 1.1) are dissolved in 50 ml of dichloromethane, 3 g (30 mmol) of triethylamine are added and 3.2 g (28 mmol) of methanesulfonyl chloride are added dropwise while stirring.

- 10 Stirring is continued for 2 hours at room temperature, and the mixture is washed with water, dried over magnesium sulfate and evaporated down under reduced pressure. The residue is taken up in dimethylformamide and the solution is added dropwise at 0°C to a suspension of 12.9 g (75 mmol) of 4,6-dimethoxypyrimidine-2-
- 15 thiol and 8.4 g (100mmol) of sodium bicarbonate in 100 ml of dimethylformamide. After stirring has been carried out for 2 hours at room temperature and for a further 2 hours at 60°C, the mixture is poured onto 1 l of ice water and the resulting precipitate is filtered off with suction. After drying, 3.2 g of
- 20 a white powder remain.

Yield: 29 % (diastereomer mixture 1:1)

The compounds stated in Table 2 were prepared similarly to the

25 above examples.

30

35

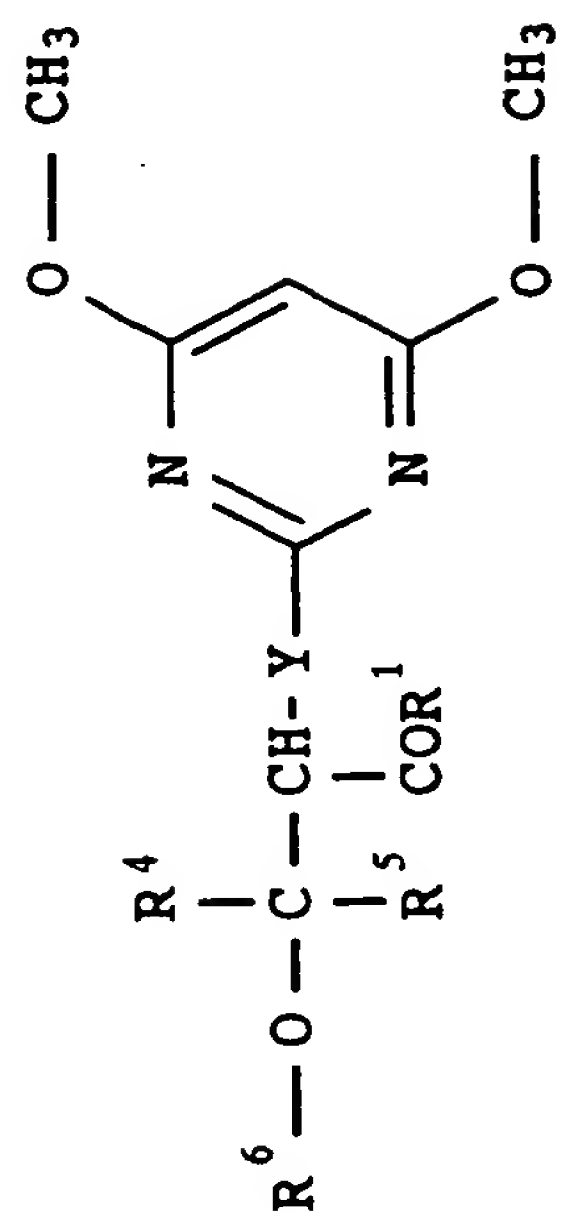
40

45

28

T290X

Table 2



No.	R ⁶	R ⁴	R ⁵	Y	R ¹	Diastereomers	Mp. (°C)
2.1	Benzyl	Phenyl	Methyl	O	OCH ₃	1:1	115-117
2.2	Benzyl	Phenyl	Methyl	O	OH	3:2	165 (decomp.)
2.3	Benzyl	Phenyl	Methyl	S	OCH ₃	1:1	
2.4	Benzyl	Phenyl	Methyl	S	OH		
2.5	Methyl	2-Fluorophenyl	Methyl	O	OCH ₃	1:1	126-128
2.6	Methyl	2-Fluorophenyl	Methyl	O	OH	2:1	185-186
2.7	Methyl	3-Methoxyphenyl	Methyl	O	OCH ₃	1:0 (5:1)	131-132 (93-95)
2.8	Methyl	3-Methoxyphenyl	Methyl	O	OH	1:0	187-189
2.9	Methyl	4-i-Propylphenyl	Methyl	O	OCH ₃		
2.10	Methyl	4-i-Propylphenyl	Methyl	O	OH		
2.11	Methyl	2-Methylphenyl	Methyl	O	OCH ₃	3:1	122-124
2.12	Methyl	2-Methylphenyl	Methyl	O	OH	1:1	135-137
2.13	Methyl	3-Methylphenyl	Methyl	O	OCH ₃	1:1	105-110

No.	R ⁶	R ⁴	R ⁵	Y	R ¹	Diastereomers	Mp. (°C)
2.14	Methyl	3-Methylphenyl	Methyl	O	OH	1:1	130-132
2.15	Methyl	4-Methylphenyl	Methyl	O	OCH ₃	1:1	99-102
2.16	Methyl	4-Methylphenyl	Methyl	O	OH	1:1	145-147
2.17	Methyl	4-Bromophenyl	Methyl	O	OCH ₃	1:0	148-150
2.18	Methyl	4-Bromophenyl	Methyl	O	OH	1:0	189-190
2.19	Methyl	2-Furyl	Methyl	O	OCH ₃		
2.20	Methyl	2-Furyl	Methyl	O	OH		
2.21	Methyl	3-Furyl	Methyl	O	OCH ₃		
2.22	Methyl	3-Furyl	Methyl	O	OH		
2.23	Methyl	2-Thienyl	Methyl	O	OCH ₃		
2.24	Methyl	2-Thienyl	Methyl	O	OH		
2.25	Methyl	2-Pyridyl	Methyl	O	OCH ₃	2:1	oil
2.26	Methyl	2-Pyridyl	Methyl	O	ONa		175-176
2.27	Methyl	3-Pyridyl	Methyl	O	OCH ₃		
2.28	Methyl	3-Pyridyl	Methyl	O	OH		
2.29	Methyl	4-Pyridyl	Methyl	O	OCH ₃		
2.30	Methyl	4-Pyridyl	Methyl	O	OH		
2.31	Methyl	3-Chlorophenyl	Methyl	O	OCH ₃		
2.32	Methyl	3-Chlorophenyl	Methyl	O	OH		
2.33	Methyl	2-Thiazolyl	Methyl	O	OCH ₃		
2.34	Methyl	2-Thiazolyl	Methyl	O	OH		
2.35	Methyl	3-Isoxazolyl	Methyl	O	OCH ₃		
2.36	Methyl	3-Isoxazolyl	Methyl	O	OH		

No.	R ⁶	R ⁴	R ⁵	Y	R ¹	Diastereomers	Mp. (°C)
2.37	Methyl	4-Imidazolyl	Methyl	O	OCH ₃		
2.38	Methyl	4-Imidazolyl	Methyl	O	OH		
2.39	Methyl	2-Pyrazolyl	Methyl	O	OCH ₃		
2.40	Methyl	2-Pyrazolyl	Methyl	O	OH		
2.41	Benzyl	4-Chlorophenyl	Methyl	O	OCH ₃	1:1	112-114
2.42	Benzyl	4-Chlorophenyl	Methyl	O	OH		
2.43	i-Propyl	2-Fluorophenyl	Methyl	O	OCH ₃	4:1	115-120
2.44	i-Propyl	2-Fluorophenyl	Methyl	O	OH	2:1	143-145
2.45	Methyl	4-Fluorophenyl	Methyl	O	OCH ₃	1:1	122-125
2.46	Methyl	4-Fluorophenyl	Methyl	O	OH	3:1	170-172
2.47	Benzyl	3-Methylphenyl	Methyl	O	OCH ₃	1:1	94- 95
2.48	Benzyl	3-Methylphenyl	Methyl	O	OH	1:1	154-156
2.49	Methyl	4-Chlorophenyl	Methyl	O	OCH ₃	1:1	125-127
2.50	Methyl	4-Chlorophenyl	Methyl	O	OH	5:1	206-207
2.51	Methyl	Phenyl	Ethyl	O	OCH ₃	1:0	95-100
2.52	Methyl	Phenyl	Ethyl	O	OH	1:0	140-142
2.53	Benzyl	4-Fluorophenyl	Methyl	O	OCH ₃	1:1	95- 98
2.54	Benzyl	4-Fluorophenyl	Methyl	O	OH	4:1	153-154
2.55	4-Fluorobenzyl	Phenyl	Methyl	O	OCH ₃	1:0	152-153
2.56	4-Fluorobenzyl	Phenyl	Methyl	O	OH	7:3	160-162
2.57	4-Bromobenzyl	Phenyl	Methyl	O	OCH ₃	9:1	158-160
2.58	4-Bromobenzyl	Phenyl	Methyl	O	OH	1:0	203-204
2.59	Benzyl	2-Fluorophenyl	Methyl	O	OCH ₃	1:0	129-130

No.	R ⁶	R ⁴	R ⁵	Y	R ¹	Diastereomers	Mp. (°C)
2.60	Benzyl	2-Fluorophenyl	Methyl	O	OH	1:0	200-201
2.61	Benzyl	4-Bromophenyl	Methyl	O	OCH ₃	1:1	78- 79
2.62	Benzyl	4-Bromophenyl	Methyl	O	OH	1:1	156-158
2.63	Benzyl	4-Methylphenyl	Methyl	O	OCH ₃	1:1	oil
2.64	Benzyl	4-Methylphenyl	Methyl	O	OH	4:1	158-159
2.65	Benzyl	Phenyl	Ethyl	O	OCH ₃	1:0	110-112
2.66	Benzyl	Phenyl	Ethyl	O	OH	1:0	92- 93
2.67	Ethyl	4-Methylphenyl	Methyl	O	OCH ₃	1:0	117-119
2.68	Ethyl	4-Methylphenyl	Methyl	O	OH	1:1	oil
2.69	Methyl	2-Furyl	H	O	OCH ₃	1:1	oil
2.70	Methyl	2-Furyl	H	O	OH	1:1	oil
2.71	4-Chlorobenzyl	Phenyl	Methyl	O	OCH ₃	1:0	172-174
2.72	4-Chlorobenzyl	Phenyl	Methyl	O	OH	1:0	60- 61
2.73	2-Butyl	4-Bromophenyl	Methyl	O	OCH ₃	-	104-106
2.74	2-Butyl	4-Bromophenyl	Methyl	O	OH	1:0	153-154
2.75	n-Propyl	4-Fluorophenyl	Methyl	O	OCH ₃	9:1	119-120
2.76	n-Propyl	4-Fluorophenyl	Methyl	O	OH	9:1	104-105
2.77	Methyl	3-Nitrophenyl	Methyl	O	OCH ₃	1:1	101-102
2.78	Methyl	3-Nitrophenyl	Methyl	O	OH	1:1	165-172
2.79	Methyl	4-Trifluorophenyl	Methyl	O	OCH ₃	1:0	112-113
2.80	Methyl	4-Trifluorophenyl	Methyl	O	OH	4:1	68- 70
2.81	Methyl	3-Thienyl	H	O	OCH ₃	1:1	80- 82
2.82	Methyl	3-Thienyl	H	O	OH	1:1	oil

No.	R ⁶	R ⁴	R ⁵	Y	R ¹	Diastereomers	Mp. (°C)
2.83	4-Chlorobenzyl	Phenyl	Methyl	O	OCH ₃	0:1	112-113
2.84	4-Chlorobenzyl	Phenyl	Methyl	O	OCH ₃	0:1	60- 61
2.85	Methyl	Phenyl	Ethyl	O	OCH ₃	1:3	125-130
2.86	Methyl	Phenyl	Ethyl	O	OH	0:1	133-135
2.87	Benzyl	3-Methoxyphenyl	Methyl	O	OCH ₃	3:1	86- 87
2.88	Benzyl	3-Methoxyphenyl	Methyl	O	OH	1:0	155
2.89	Benzyl	3-Methoxyphenyl	Methyl	O	OH	0:1	138-140
2.90	2-Phenylethyl	Phenyl	Methyl	O	OH	1:0	147-149
2.91	Methyl	3-Furyl	H	O	OCH ₃	1:1	oil
2.92	Methyl	3-Furyl	H	O	OH	1:1	131-135
2.93	3-CF ₃ -benzyl	Phenyl	Methyl	O	OCH ₃	2:1	151-152
2.94	3-CF ₃ -benzyl	Phenyl	Methyl	O	OH	1:1	oil
2.95	2-Fluorobenzene	Phenyl	Methyl	O	OCH ₃	2:1	170-173
2.96	2-Fluorobenzene	Phenyl	Methyl	O	OH	1:0	160-162
2.97	2-Fluorobenzene	Phenyl	Methyl	O	OH	1:3	138-141
2.98	3-Fluorobenzyl	Phenyl	Methyl	O	OCH ₃	1:1	81- 86
2.99	3-Fluorobenzyl	Phenyl	Methyl	O	OH	4:1	195-197
2.100	3-Fluorobenzyl	Phenyl	Methyl	O	ONa	3:1	250-260
2.101	4-Fluorobenzyl	Phenyl	Methyl	O	OCH ₃	1:1	112-115
2.102	4-Fluorobenzyl	Phenyl	Methyl	O	OH		

Use examples:

The herbicidal action of the 3-(het)arylcarboxylic acid derivatives of the general formula I could be demonstrated by greenhouse experiments:

The culture vessels used were plastic flowerpots containing loamy sand with about 3.0 % of humus as a substrate. The seeds of the test plant were sown separately according to species.

In the preemergence treatment, the active ingredients suspended or emulsified in water were applied directly after sowing by means of finely distributing nozzles. The vessels were lightly sprinkler-irrigated in order to promote germination and growth and were then covered with transparent plastic covers until the plants had begun to grow. This covering ensures uniform germination of the test plants, unless this has been adversely affected by the active ingredients.

20

For the postemergence application, the test plants are grown to a height of growth of from 3 to 15 cm, depending on the form of growth, before being treated with the active ingredients suspended or emulsified in water. For this purpose, the test plants are either sown directly and grown in the same vessels or first grown separately as seedlings and transplanted into the test vessels a few days before the treatment. The application rate for the postemergence treatment is 0.125 or 0.06 kg/ha of a.i.

30 The plants were kept at 10 to 25°C or 20 to 35°C, according to species. The experimental period is extended over from 2 to 4 weeks. During this time, the plants were tended, and their reaction to the individual treatments was evaluated.

35 Evaluation was based on a scale from 0 to 100. 100 means no emergence of the plant or complete destruction of at least the above-ground parts and 0 means no damage or normal course of growth.

The plants used in the greenhouse experiments consisted of the following species:

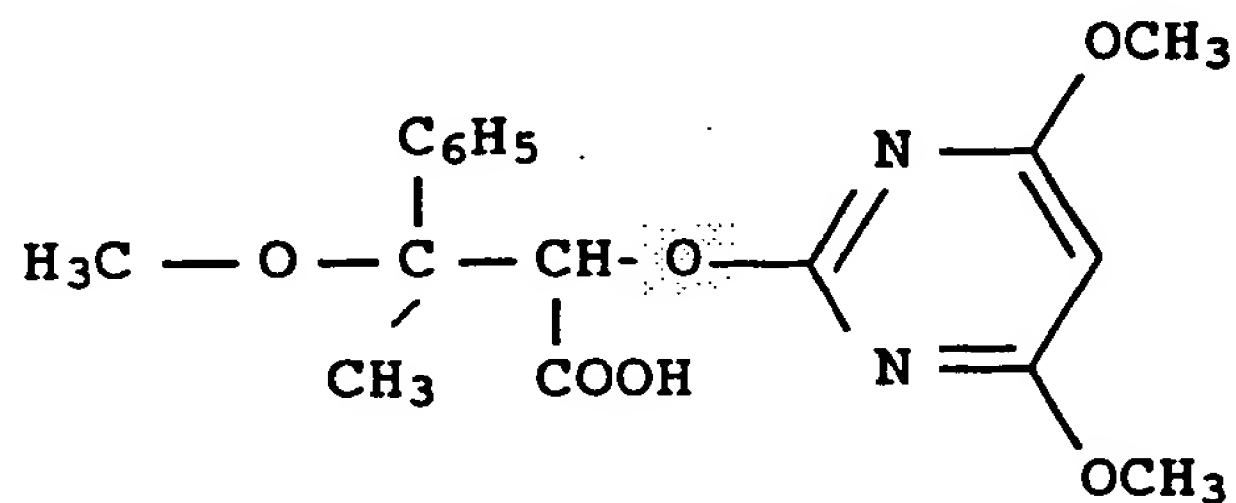
45

34

	<u>Botanical Name</u>	<u>Common Name</u>	<u>Abbreviation</u>
	Gossypium hirsutum	Cotton	GOSHI
	Oryza sativa	Rice	ORYSA
5	Triticum aestivum	Summer wheat	TRZAS
T350X	Alopecurus myosuroides	Slender foxtail	ALOMY
	Amaranthus retroflexus	Redroot pigweed	AMARE
	Brachiaria platyphylla	-	BRAPP
	Chenopodium album	Common lambsquarters	CHEAL
10	Sesbania exaltata	Hemp susbania	SEBEX
	Setaria faberii	Giant foxtail	SETFA
	Setaria viridis	Green foxtail	SETVI
	Solanum nigrum	Black nightshade	SOLNI
15	Veronica spp.	Speedwell species	VERSS

20 The results listed in Table A show the superior herbicidal action and the better selectivity of the novel compound No. 2.2 in comparison with the comparative substance A disclosed in EP-A 409 368

25



A

35

40

45

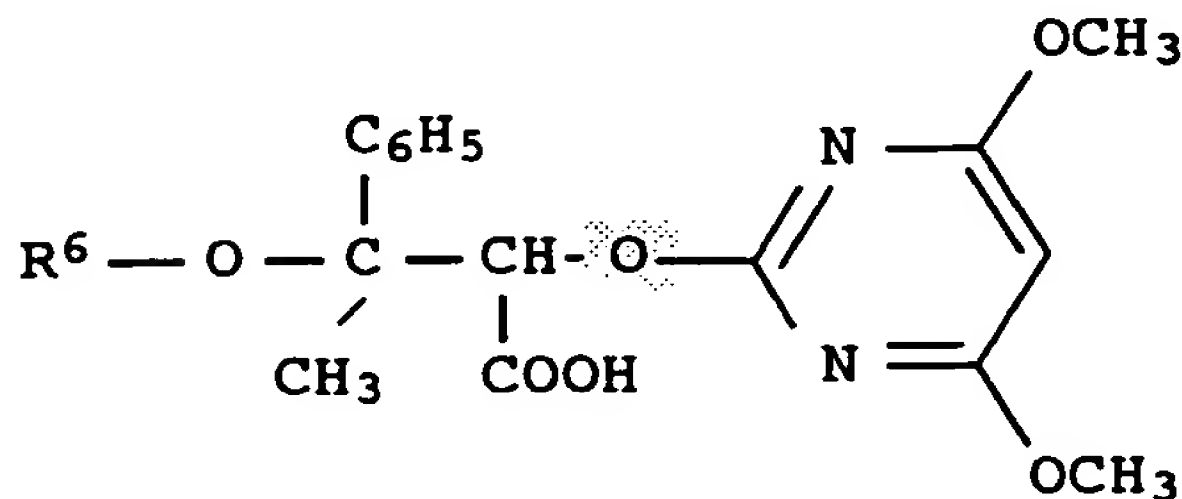
35

Table A

Examples of the control of undesirable plants and selectivity in the example crop cotton with postemergence application of 0.125 or 0.06 kg/ha of a.i. in the greenhouse.

5

10



15

R⁶
Example No. 2.2

CH₃
A

	Test plants	Damage in %		Damage in %	
		0.125 kg/ha	0.06 kg/ha	0.125 kg/ha	0.06 kg/ha
20	GOSHI	10	5	35	20
	SEFTA	100	100	75	70
	SETVI	100	98	80	60
	AMARE	98	98	100	75
25	SOLNI	100	100	98	90

At application rates of 5 kg/ha to 0.25 kg/ha, compounds No. 2.84, 2.16, 2.52, 2.86 and 2.25 showed good herbicidal activity. Compounds No. 2.84 and 2.16 simultaneously showed very good selectivity in the example crop cotton. In addition, Example No. 2.16 was also selective in rice. Example 2.52 was well tolerated by the crop summer wheat.

35

40

45

36